THE EFFICIENT, LARGE SCALE SEPARATION OF COAL MACERALS

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INTRODUCTION

For fundamental work on the chemical structure of coal, one of the first tasks that should be performed on a coal sample is to ensure that it is as homogeneous as is currently possible. This should require, at the very least, a petrographic analysis, and in many cases a subsequent separation to regulate the quality of the maceral or maceral group, even if the coal sample is optically monomaceral. Dyrkacz et al. have shown that even "pure" vitrinite shows a density distribution, which is, in part, related to differences in chemistry within the vitrinite maceral group.[1-3] However, despite the probability that experimental data may suffer from poorly characterized coal samples, it is not traditional practice to be concerned with the maceral separation of coal. The primary reason for this is that maceral separation is considered to be tedious and time-consuming. There is some truth in this statement, but the underlying question which should be asked is what is more important, the credibility and general applicability of the research data, or the additional time required to do a physical separation.

In our continuing efforts in the area of maceral separation, we have recognized the need for a process to supply relatively large amounts of macerals as rapidly as possible. Earlier we reported some initial work using combined sink/float and density gradient centrifugation (DGC) or continuous flow centrifugation and DGC.[4] These early results indicated that continuous flow separation was somewhat effective, but beset with equipment specific difficulties.

Nevertheless, there are several notable advantages in using continuous flow centrifugation for maceral separation. First, the coal particles can be in a highly dilute suspension, which reduces particle-particle interactions. Second, large amounts of material can be separated; the major limitation being the capacity of the rotor. Third, the separation efficiency is higher. Unlike batch sink/float centrifuge operations, there are less cross-contamination problems with removal of the light and heavy particles, since the light phase is continuously removed. Lastly, the separation is fast. To produce an equivalent amount of purified coal material, much less manipulation is necessary to achieve separation compared to batch sink/float.

With all of these advantages in mind, we have again turned our investigations to continuous flow centrifugation for maceral separations. However, this time we are using a centrifuge specifically designed for such work. We report here our initial investigations on the separation of the maceral groups from Lewiston-Stockton coal from the Argonne Premium Coal Sample Program (APCS-7).

EXPERIMENTAL

Coal Pre-treatment. The APCS-7 coal (-100 mesh) was ground to 1-2 microns average particle size using a Fluid Energy Mill (Sturtevant). The coal was then demineralized using HCl and HF as we have previously reported.[5]

Continuous Flow Centrifugation Procedure. A continuous flow centrifuge (CEPA-LE Laboratory centrifuge, Carl Padberg Zentrifugenbau GmbH; U.S. supplier: New Brunswick Scientific Co., Inc.) with a model "K" clarifier rotor was used for the work reported here. A Sharples model T-1, (PenWalt Corp.), with a 1-H clarifier rotor was also used for some early work. Rotor speed was measured with a Xenon strobe lamp and maintained at 37000 ± 2000 rpm. A peristaltic pump (Masterflex, Model 7520-00, Cole-Parmer) was used to pump the coal slurry through the spinning rotor at a flow rate of 160 mL/min. Before the coal slurry was fed into the rotor, clear solution was used to fill the rotor. Clear solution was also used after the separation to ensure that all the floating coal had been removed. The rotor effluent and deposit were filtered, washed with water, dried and weighed. When the rotor was stopped, fluid that remaining in the spinning rotor drained out. This material was collected and analyzed separately.

DGC Monitoring of the Continuous Flow Separation. Aliquots of the three fractions: effluant (float), deposit (sink) and rotor liquid, derived from the continuous flow centrifuge separation were analyzed by the analytical density gradient centrifugation procedures of ref. [5].

RESULTS

The continuous flow centrifuge that we employed is commonly used for separation of biological materials, such as the harvesting of cells or other biological particulates. This centrifuge is a much simpler design than we used previously.[4] The heart of the centrifuge is the rotor which consists of a simple rotating hollow cylinder which narrows to an open tube at the bottom and has holes drilled perpendicular to the main axis for the fluid to exit at the top. The expelled effluant is retained by an encircling collector ring. Fluid is injected into the rotor at the bottom through a nozzle centered in a lower bearing assembly. A series of radial vanes within the bottom of the rotor help accelerate the fluid to the rotor velocity. From this description, it is obvious that the CFC process is not truly continuous, since once the rotor deposit nearly fills the rotor, operation must be suspended long enough to empty the rotor. However, this represents only a minor inconvenience when compared to the manipulations involved in a sink/float centrifuge separation.

The coal sample that was chosen for our investigations was the Lewiston-Stockton coal (APCS-7) from West Virginia. This coal is reported to have a high proportion of all three maceral groups. Our own petrographic analysis shows this coal to contain 11.5% liptinite, 72.8% vitrinite and 15.6% inertinite.

There are two ways to analyze the efficiency of the continuous flow procedure. One of the more common approaches is to petrographically analyze the samples generated in the CFC separation. However, we know that the maceral groups have particle density distributions that naturally overlap each other.[2] Thus, the presence of more than one maceral type in a sink or float fraction does not necessarily translate to a bad separation. Since petrographic analysis is not

able to make such fine distinctions, we chose to use density gradient centrifugation (DGC) to determine the true state of the separated material.

To effectively use DGC, it is first necessary to obtain the density distribution of the unseparated coal. Figure 1 represents the separation and maceral analysis of a two gram sample of APCS-7 coal, using a CsCl/Brij-35 aqueous gradient. This maceral distribution pattern is consistent with other coals of similar rank.[2,4]

Two CFC separations were done on APCS-7 using separate samples. The density cuts were made at 1.232 and 1.332 g cm^{-3} using CsCl/Brij-35 aqueous solutions. From Figure 1, these densities are near the density points where equal amounts of either liptinite/vitrinite or vitrinite/inertinite particles should be present. The concentration of coal in the feed slurry was 40 g/L. This amount is not the highest slurry concentration that can be used, but instead represents a conservative experiment to demonstrate the separation. However, even this slurry concentration is still much higher than we would recommend for optimum resolution in simple sink/float maceral separations.

Once the separations were completed, the coal in each fraction was isolated by filtration, washed, dried and weighed. Figure 2 represents the sum of all the observations for these two individual separations. The data on the sink/float fractions, as we have already indicated, were derived from analytical DGC on very small amounts (2 mg) of each fraction. The vertical bars on the plots represent the densities of the solutions. Following any particular density distribution of a sink or float fraction (lower two plots), anything passing the vertical line represents cross-contamination. As can be seen some of the fractions are better than 90% disengaged. This result approaches the limit of analytical DGC to probe the CFC separation, since there is some unavoidable maceral band spreading which can give the false impression of contamination. On the other hand, there are some fractions which show substantial cross-contamination. The liptinite/vitrinite+inertinite separation shows a strong bimodal distribution in the float fraction, as does the sink fraction in the liptinite+vitrinite/inertinite separation.

The curves in the lower two plots of Figure 2 oversimplify a more complicated experimental reality, which more critically explains the reason for some fractions showing poorer maceral resolution. The sink data in Figure 2 are actually composed of two separate fractions. Three fractions are actually collected from each run: the float, which exits the rotor during the run, the sink, which is the deposit on the rotor wall, and a third portion, which is obtained from the solution left in the rotor when the run is completed. This additional fraction is collected once the velocity of the rotor decreases below a certain limit. The centrifugal force becomes to low to retain the fluid, and it drains out the bottom of the rotor. It is the sum of this material and the material deposited on the rotor wall, which is shown in Figure 2. Figures 3 and 4 show all three fractions from both density cuts. Each density distribution curve has been normalized to the highest absorbance value (roughly proportional to mass). Notice that all the fractions labeled as sink (material on rotor wall) are actually well separated. The fraction labeled as rotor drainage (Rtr. Drng.) exhibits a high degree of cross-contamination in both runs. Table 1 provides the separation data on the purity of the fractions; the data is derived by integrating the analytical DGC results before and after the solution density cut line shown in either Figures 2 or 3. Without the inclusion of the rotor drainage material (which can account for approximately 50% of the sink material

collected), the material deposited on the rotor wall shows excellent resolution from float material.

We have attributed the behavior of this rotor drainage fraction to the sum of several processes:

1. When the solution in the rotor drains out at the end of the run, some of the material from the rotor wall is unavoidably carried away in this process. At this time we cannot say how much. The level of contamination with sink material may be high because in our tests relatively small amounts of coal (20 grams) are being separated and are being deposited in a narrow area of the rotor.

2. The coal particles have a range of particle size from about 0.5 to 6 microns. The very fine particles may not have time to separate during their passage through the rotor and may be held up in the rotor.

3. Some of the material cannot be separated because it is at or very close to the same density as the solution density.

We have examined several of the float contaminations in our sink fractions under the microscope, and indeed have found that finer material is present in much higher concentration than in the feed. In the case of the liptinite/vitrinite+inertinite separation in Figure 3 the float fraction also shows a large contamination peak. We have determined that the high density peak is due to the presence of extremely fine particles (< 1 micron). This fact suggests that the high density peak does not represent the true amount of material. We have observed previously that fine particles may give rise to a much larger absorbance than larger particles due to greater scattering. The purity in this case should be considered as a minimum enrichment.

DISCUSSION

We believe that the separation of macerals by continuous flow centrifugation offers a simple technique for the large scale separation of macerals. With relatively little cost (~ $10K), it provides an opportunity for obtaining quite pure maceral fractions. Although we have not completely worked out all the nuances of this separation system, we believe that the problems we have indicated can be minimized to pose only minor inconvenience.

We cannot say that this system completely bypasses the diasagreeable tedium or time involved in separating macerals, nor will it by itself overcome the mental inertia required to make maceral separation an accepted necessary fact in fundamental coal science. However, we find our particular brand of continuous flow centrifugation is considerably faster than sink/float separation, can provide a good quality product with even one separation cycle, and permits the handling of more material than a conventional sink/float centrifuge separation.

ACKNOWLEDGMENTS

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TABLE 1. Analysis of Continuous Flow Centrifugation Separation by Analytical Density Gradient Centrifugation.

	Percent Purity of Fraction from DGC		
Float	Rotor Drainage	Rotor Deposit	Total Sink
Cut Density = 1.232 g cm^{-3}			
47.9	95.7	99.6	98.6
Cut Density = 1.332 g cm^{-3}			
97.4	59.3	97.6	79.4

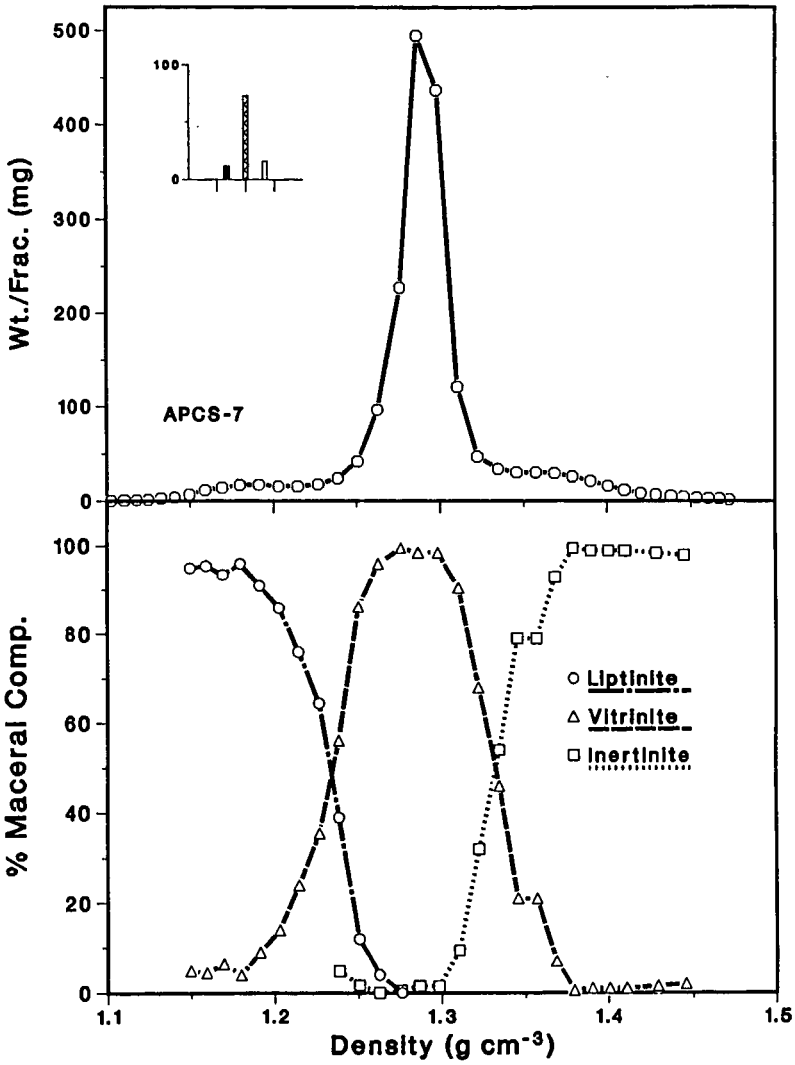

Figure 1. Maceral density distribution of APCS-7 coal obtained by DGC. Lower plot is the maceral analysis of selected density fractions. All densities are at 25°C.

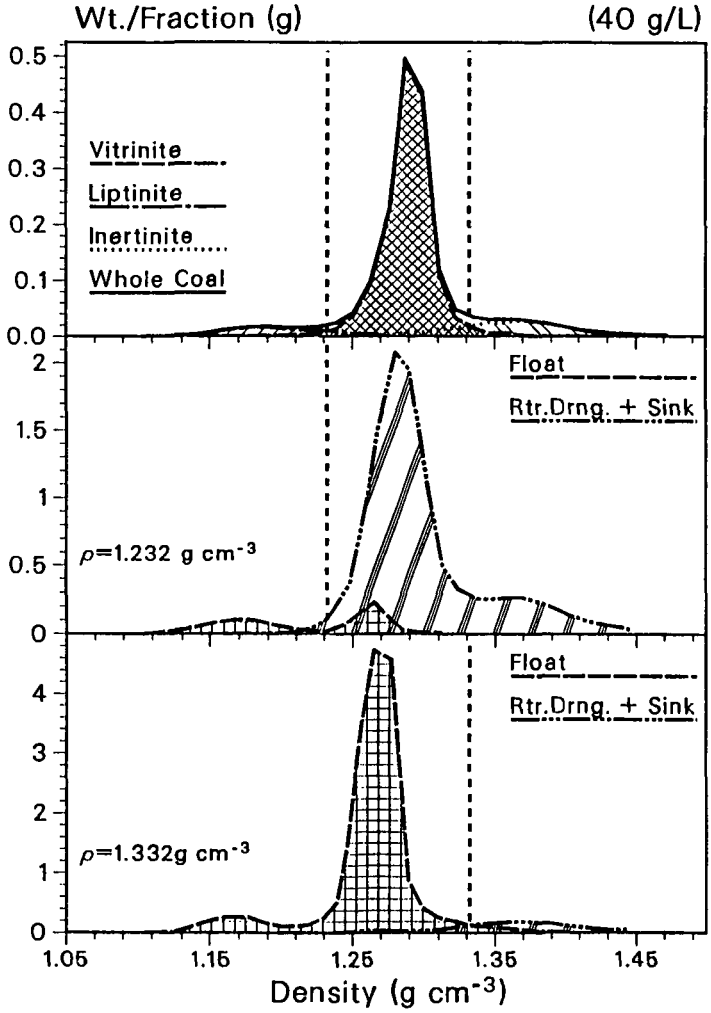

Figure 2. Top: Maceral density distributions of APCS-7 showing the actual weight distribution of each maceral group. Middle: DGC separations of float and sink CFC fractions for removing liptinite from vitrinite + inertinite. Bottom: DGC separations of float and sink CFC fractions for removing vitrinite + liptinite from inertinite. Absorbance is roughly proportional to weight.

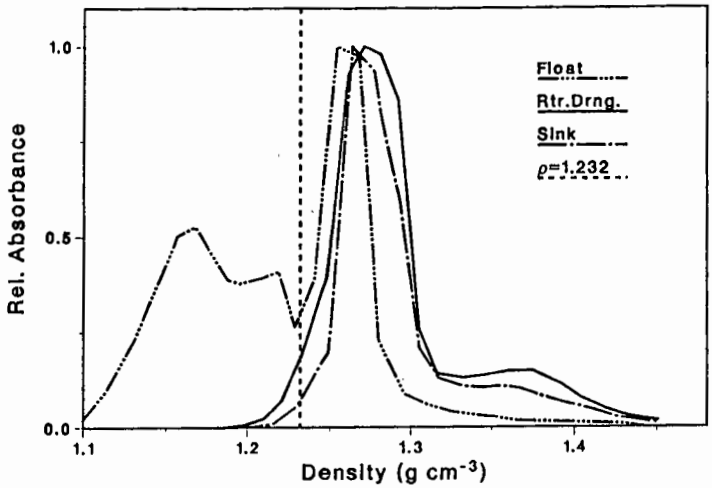

Figure 3. Detailed DGC pattern for the three collected CFC fractions for liptinite removal. All distributions have been normalized to the highest peak in each individual fraction.

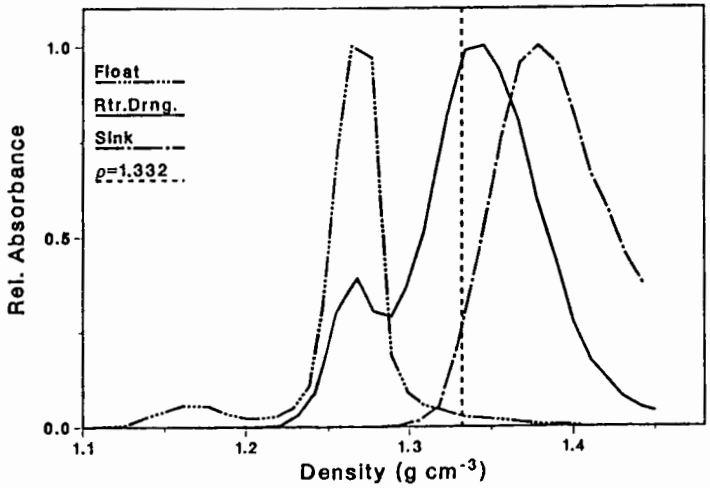

Figure 4. Detailed DGC pattern for the three collected CFC fractions in inertinite removal. All distributions have been normalized to the highest peak in each individual fraction.